

Relationships between Structure and Mechanical Properties of Rubber-Modified Epoxy Networks Cure with Dicyanodiamide Hardener

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Synopsis

Epoxy network systems based on DGEBA and dicyanodiamide (DDA) and modified with a low molecular weight rubber (CTBN) were prepared and characterized. The kinetics of the adduct formation is followed using GPC analysis. The phase separation of the rubber phase is evidenced with DSC and SEM for all samples up to 20% CTBN. The GPC analysis of the soluble fraction demonstrates a chemical modification of the network. The mechanical properties and specially the impact strength behavior are enhanced with CTBN, but exhibit a maximum for 15% CTBN. In connection with SEM of fracture surfaces, these results are discussed and both modification of the rubber morphology and decrease in crosslinking density are taken into account.

INTRODUCTION

It has long been known that the fracture toughness of thermoplastics or thermosetting resins is considerably improved with small rubber particles dispersed in the polymer.¹

The effect of the particulate elastomeric modifiers on the fracture behavior of epoxy networks was studied, previously by McGarry and co-workers² and then by different authors.³⁻⁸ These investigations have shown that when an elastomer, generally a low molecular weight carboxyl-terminated butadiene acrylonitrile copolymer (Hycar CTBN), was copolymerized with the epoxy prepolymer prior to gelation, a uniformly dispersed phase of small rubber particles was formed *in situ*. These particles, with diameter of a few microns or less, enhance the toughness of the unmodified epoxy network by several orders of magnitude. The toughening mechanism involves triaxial dilation of the rubber particles at the crack tip,² particle elongation,⁹ and plastic flow of the epoxy matrix.¹

Type and concentration of hardener, curing temperature, kind of rubber, rubber content, and initial rubber molecular weight, concentration of bisphenol A were extensively studied^{2,8} and are known to influence the composition and size of particles which, in turn, change the fracture energy.

Cyanoguanidine or dicyanodiamide (DDA) is a solid hardener with a high melting temperature (207°C) and with a poor solubility in epoxy prepolymers (0.06% at 30°C). The reaction of DDA with a diglycidyl ether of bisphenol A (DGEBA) epoxy prepolymer is very intricate.^{10,11} Even formulations with this curing agent are often used in adhesives and fiber-rein-

forced plastics; few publications report the properties of these rubber toughened epoxy networks.⁴

The aim of this work is to develop a better understanding of the ways in which rubber concentration affects the network morphology. The mechanical properties and specially the impact strength are discussed in relation with the morphology, the particle volumic fraction of rubber, and the modification of the matrix.

EXPERIMENTAL

Materials

The chemical products used in this work are listed on Table I.

Techniques

Formulations and soluble fractions were characterized by gel permeation chromatography (GPC) on a Waters apparatus with THF as elution solvent. Eluted macromolecules were observed simultaneously by refractive index (RI) and by ultraviolet absorption ($\lambda = 254$ nm).

Microcalorimetric measurements were recorded with a DSC Mettler TA3000. Dynamic mechanical properties were observed by mean of a Rheovibron RVIIB viscoelasticimeter (Toyo Baldwin) with a heating rate of $1^{\circ}\text{C min}^{-1}$ at 11 Hz. A Charpy instrumented setup¹² lead us to study the impact toughness. Scanning electron micrographs (SEM) on fracture surfaces were obtained with a JEOLT.200 apparatus.

Preparation of Samples

Curing Conditions. DGEBA is mixed, with 11 phr of DDA and 1 phr of BDMA at 60°C for 2 h, in a glass vessel under a primary vacuum.

These proportions are in agreement with a stoichiometric ratio of 1 if we assume a functionality of 4 for DDA; but, in fact, recent works indicate a more complex mechanism.^{10,11}

The final properties of the network formed depend strongly on the cure temperature.^{2,4} We have chosen a cure cycle of 1 h at 140°C ; DSC measurements show that, in these conditions, the chemical reaction is mostly ended (no exothermal effect).

The choice of this low cure temperature is to prevent possible oxidation and degradation of the CTBN.

Preparation of the Adduct. Epoxy and rubber prepolymers are pre-reacted to insure the formation of an epoxy-rubber intermediate and to promote the blending of these prepolymers before curing. The mechanism of this reaction has been discussed by Siebert and Riew¹³ and Riew et al.³

A large amount of this adduct is prepared at 85°C , with mechanical stirring under a nitrogen flow, using triphenylphosphine (0.25 phr) as catalyst. In order to have an excess of epoxy, the epoxy/carboxyl ratio is chosen to equal to 14.

To insure that all CTBN molecules are end-capped with a DGEBA molecule, we follow the advancement of the reaction by GPC. Figure 1 shown the UV and RI chromatograms for an aliquot, the pure CTBN does not

TABLE I
Chemical Products

Materials	Chemical formula	Trade mark
Epoxy pre-polymer $M_n = 380 \text{ g/mol}$		DGEBA 0164- Bakelite
Hardener DDA	$\text{NH}_2 - \text{C} \begin{array}{l} \diagup \text{N} \\ \diagdown \text{N} \end{array} - \text{C} \equiv \text{N}$	VE 2560- Bakelite
Catalyst BDMA		Fluka
Rubber CTBN $M_n = 3500 \text{ g/mol}$	$\text{HOOC} - \left[\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 \right]_6 - \left[\text{CH}_2 - \underset{\text{CN}}{\text{CH}} \right]_{10} - \text{COOH}$	Hycar CTBN 1300 × 8 Goodrich

similar to those of Wang and Zupko¹⁵ obtained on CTBN + DGEBA blends. At 140°C for all blends we have initially a one-phase system. During the cure the phase separation occurs in competition with the network formation. The two processes are responsible for the final morphology but previous work⁴ indicates that morphology development is arrested at gelation.

We determine the time at which phase separation occurs by DSC measurements with the use of 2 $T_g = 2$ phases criterion.

Reactive mixtures in caps are cured, in the DSC apparatus, for various time t , at 140°C, quenched at liquid nitrogen temperature and then analyzed. The results are shown on Figure 3 for a 15% CTBN blend.

The single glass transition exhibited on curves (c) and (d) of Figure 3 confirms that the initial system is homogeneous at 60 and at 140°C.

The glass transition temperature of a second rich-CTBN phase (T_{gR}) begins to appear after 5 min of cure at 140°C. After 10 min at 140°C the heat capacity change ΔC_p at T_{gR} becomes constant, showing that the amount of CTBN in the separate phase does not change.

In the state of our knowledge it is very difficult to know if phase separation arises before gelation or after and further investigations will be necessary.

Characterization of Soluble Parts

In order to study the chemical properties of the network we have performed the extraction of soluble parts in THF, with a Soxhlet setup. The kinetics of extraction depends strongly on the shape of the samples and on the CTBN content.

Using GPC analysis it is possible to separate the "DGEBA end-capped CTBN" peak from the other soluble products: DGEBA, DDA, and low molecular weight species (arising from the chemical reaction). Usually it is difficult to distinguish, in THF, the DGEBA peak from the DDA, but, with

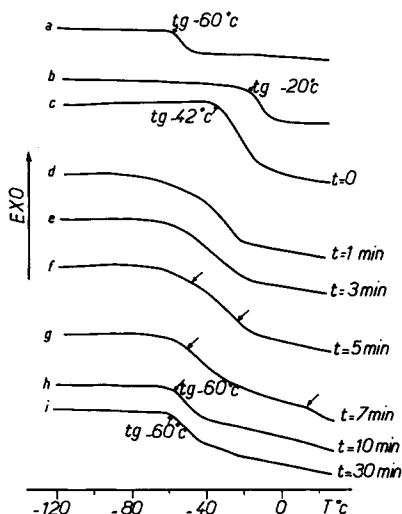


Fig. 3. DSC analysis: (a) pure CTBN; (b) pure DGEBA. Evolution of phase separation with time of cure at 140°C: (c) initial mixture 15% CTBN, mixed 2 h at 60°C; (d, e, f, g, h, i) $t = 1$ –30 min.

TABLE II
 GPC Analysis of the Soluble Parts in THF

Soluble parts (g/100 g)	% CTBN					
	0	5	10	15	17	20
DGEBA	4.4	4.8	6.2	6.9	8	14.2
DDA	0	0	0	2.5	7	15
CTBN	0	0	0	1.5	6.8	10
Total	3.2	3.2	3.4	4.0	7.3	12.1

the two-detector apparatus (cf. Techniques) it becomes easy due to the fact that the DDA does not absorb the 254 nm radiation. The results are summarized in Table II.

For the blends up to 10% CTBN, the total extraction ratio is nearly constant, DDA and DGEBA-end-capped CTBN being not pointed out.

From 15%, the soluble parts are made with all reactants and the extraction ratio is strongly increasing.

So, these experiments demonstrate that the crosslinking density of the rubber-modified epoxy networks decreases when the initial CTBN content becomes $> 15\%$. On the other hand, the amount of DGEBA-end-capped CTBN which is not linked to the network probably decreases the adhesion between the two phases.

Composition and Dimensions of the Rubber Phase

Using DSC analysis the phase separation is qualitatively shown (T_{gR} , T_{gE}) for all the samples except the 5% CTBN (Fig. 4). On the other hand, SEM (Fig. 5) shows nodular morphology even for the 5% CTBN. So we think that there is a lack of precision of DSC measurements which are not able to determine T_{gR} on this sample.

Up to 15% CTBN by weight T_{gR} is similar to those of pure CTBN, and for 17 and 20% T_{gR} is increasing due probably to the presence of DGEBA (crosslinked or not) in the rubber phase.

In order to appreciate the toughening effect due to the CTBN domains we have to estimate the volumic fraction (ϕ_v), the average diameter and

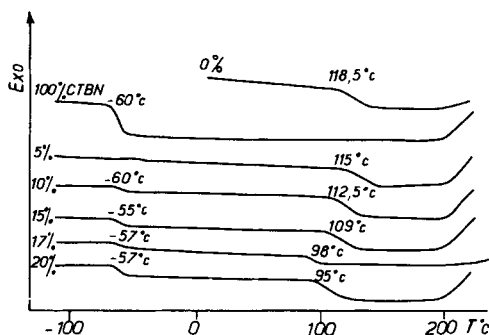


Fig. 4. DSC analysis of DGEBA-CTBN samples cured 1 h at 140°C.

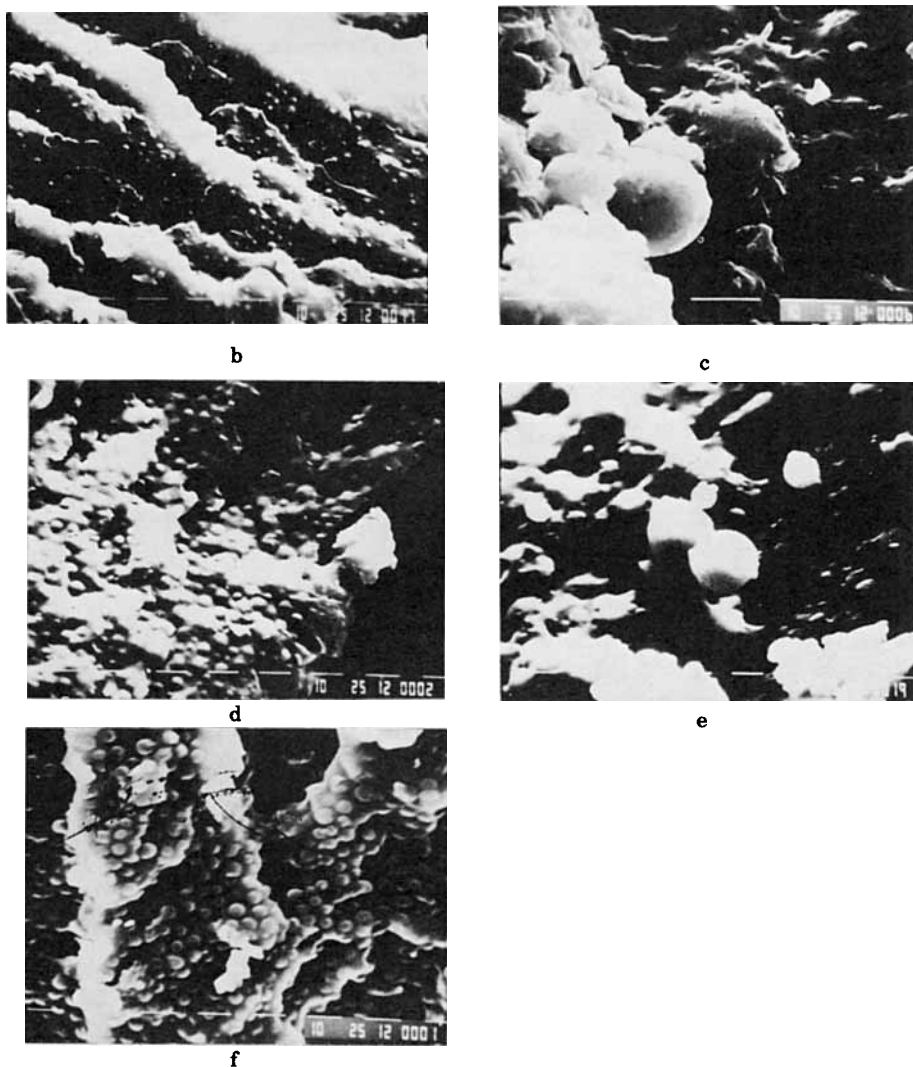


Fig. 5. Morphology of rubber-epoxy networks. SEM—scale bar = 10 μm ; (b, c, d, e, f) 5, 10, 15, 17, 20% CTBN.

the size distribution of this separate phase which are important parameters.^{1,2,4,16}

There are many well-known models and equations based on the determination of T_{gR} , T_{gE} , ΔC_p ¹⁷⁻¹⁹ to determine the relative compositions. But the lack of precision of DSC analysis, the presence of DGEBA ($T_g = -20^\circ\text{C}$) or epoxy network ($T_g = 118^\circ\text{C}$), in this rubber phase lead us to calculate an order of magnitude of ϕ_r only with the simple equation of Fox.¹⁷ The results are summarized in Table III; calculations are made with T_g CTBN = -60°C , T_g pure network = 118°C , and assuming the density of pure CTBN phase is equal to those of liquid CTBN (0.948).

The quantitative evaluation of phase separation with SEM is rather difficult, considering that the fracture is not plane, and the crack, certainly,

TABLE III
Influence of CTBN Content on Average Diameters, Dispersion, and Volumic Fractions of the Rubber Phase

% CTBN	5	10	15	17	20
Average diameter \bar{D} (μm)	1.7	2.2	3.5	2.5-15	5-20
$\Delta\bar{D}$ (μm) (estimated)	0.2	0.3	0.5		
ϕ_v (SEM) (%)	1.5	4.4	9.6		
ϕ_v (DSC) (%)	4.3	10	15	13.5	16

does not reveal all the particles. The average apparent diameters and the estimate dispersion are listed in Table III.

We notice relatively small diameters for blends up to 15% with a narrow dispersion (see Fig.5) and, the opposite for 17 and 20% CTBN, bigger particles with a broad dispersion.

These two methods show that the degree of phase separation in the rubber phase is very important up to 15% and less after.

Composition of the Epoxy Matrix Phase

The presence of CTBN in the epoxy matrix phase is evidenced by the continuous lowering of T_{gE} from 118.5 to 95°C (Fig. 4). Relaxation spectra at high temperatures are shown in Figure 6.

We observe a decrease of the modulus with the CTBN content. The loss tangent peaks associated with the glass transitions observed by DSC show a strong broadening of the relaxation times distribution at 17 and 20% CTBN. These observations may demonstrate that the rubber-epoxy interphase is not the same. The important amount of soluble fractions proves that the epoxy matrix phase is strongly affected. This broadening would be

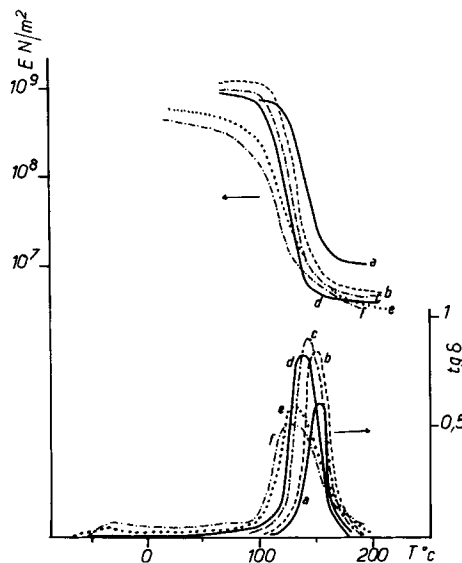


Fig. 6. Influence of CTBN content on dynamic mechanical properties: (a, b, c, d, e, f) 0, 5, 10, 15, 17, 20% CTBN.

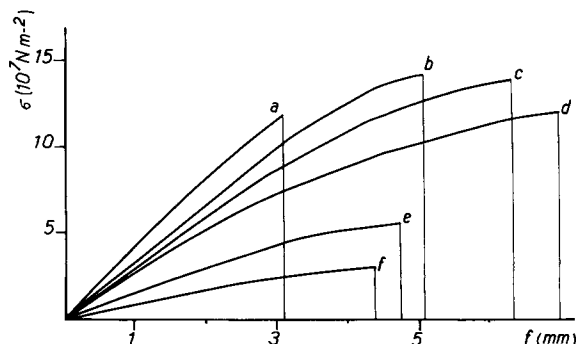


Fig. 7. Three points bending test at room temperature. Influence of the CTBN content on stress-deflection curves; (a, b, c, d, e, f) 0, 5, 10, 15, 17, 20% CTBN.

due to the composition heterogeneity and the decrease of the network cross-linking degree.

Mechanical Properties and Toughening Effect

A strong, nonlinear toughening effect due to the presence of rubber particles is evidenced using a three-point bending test (Fig. 7) and a Charpy instrumented impact test (Fig. 8). The impact resilience of the pure epoxy matrix (10 kJ/m^2) becomes 33 kJ/m^2 at the maximum which corresponds to 15% of initial CTBN. The use of an instrumented setup¹² allows us to analyze the absorbed energy. As with Adams and Wu²⁰ the total energy may be separate in two parts: the first, W_i , the energy of initiation (work done to reach the greatest applied stress), and the second W_p , the energy of propagation.

The balance between W_i and W_p gives us information about the mechanism of deformation and the absorption of energy during the impact. We

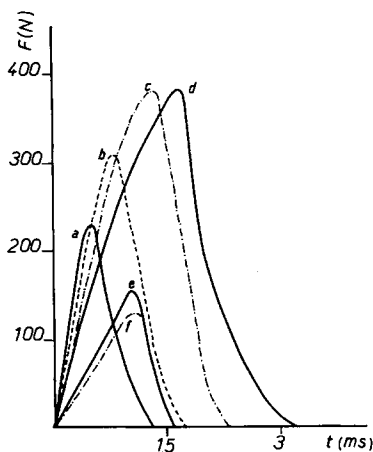


Fig. 8. Charpy instrumented impact test at room temperature. Load-time curves: (a, b, c, d, e, f) 0, 5, 10, 15, 17, 20% CTBN.

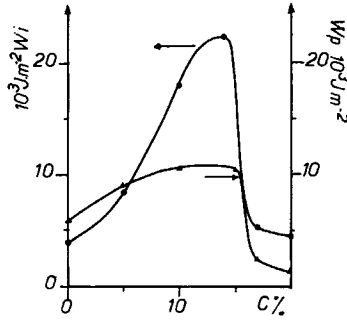


Fig. 9. Evolution of the energy of initiation (w_i) and propagation (w_p) for CTBN-modified epoxies.

observe (Fig. 9) only small variations in W_p , but we remark that the toughening effect is mainly due to the increase in W_i , with a maximum at 15%.

This phenomenon is interpreted^{1,6} with the stress concentration effect of the rubber particles associated with the creation of crazes (stress whitening is observed), which slows down the apparition of cracks, and thus a greater stress may be reached at a greater deflection.

DISCUSSION AND CONCLUSION

It is usually admitted that there is a toughening effect up to 20% of rubber and a flexibilizing one between 20 and 50%.⁵

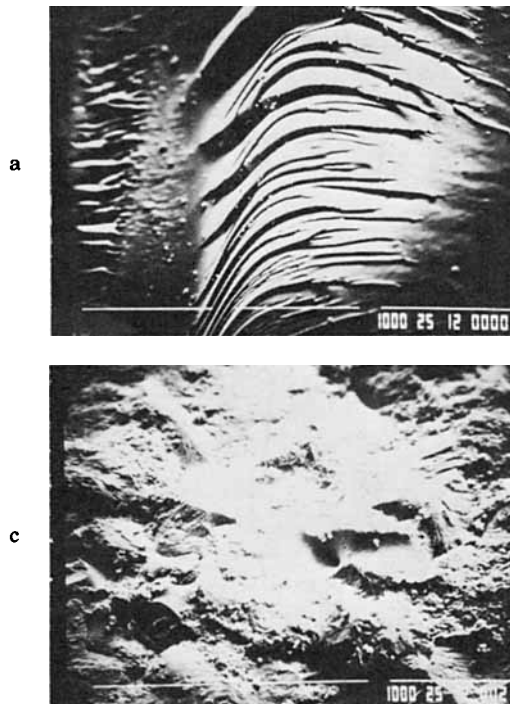


Fig. 10. Influence of CTBN on SEM fracture surfaces; (a, c) 0,10%; scale bar = 1mm.

A linear reinforcement with particle volumic fraction is found by several authors^{16,21} and the existence of a maximum is described by Bascom et al.⁶ and Rink et al.²²

Here, in this study with the particulate system DGEBA-*DDA*, we observe an optimum of the chemical properties for 15% of initial CTBN.

This toughening effect, according to many authors, is due to the presence of small rubber particules (between 1.7 and 3.3 μm) with a narrow size distribution. The DSC analysis and relaxation spectra show that the rubber domains contain mainly CTBN; the network is not too modified by the presence of CTBN, as shown by the nearly constant extraction ratio. This reinforcement is well exhibited on fracture surfaces.

Figure 10 shows the fracture surface of pure epoxy network with fibrils in steplike fracture.⁷ This failure process is strongly modified by rubber particles and rough fracture surfaces are exhibited. In Figure 11 we can see cracks between rubber particles and plastic deformation zones around the cavities.

The observations are in good agreement with the evolution of W_i .

Beyond 15% we don't observe an improvement of the mechanical properties but a dramatic fall, and this may be explained considering both the change in the rubber particles morphology and size and the structural modifications of the network.

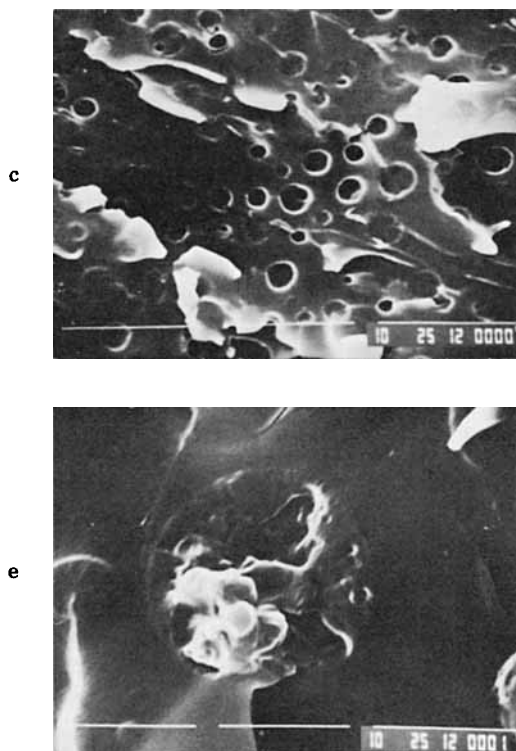


Fig. 11. Details of SEM fracture surfaces near rubber particles; (c, e) 10, 17% CTBN; scale bar = 10 μm .

For 17 and 20% of CTBN the particles size increases but especially the size distribution (Figs. 5(e),(f). As indicated by the decrease of T_{gR} DGEBA macromolecules, linear, grafted, or crosslinked, are present in the rubber domain, giving such big and heterogeneous particles. An example of the complex structure of a rubber particle is shown on Figure 11(e). This micrograph reveals that the particle is not pulled out but cut by the crack.

As demonstrated by the extraction ratio, the degree of crosslinking of the network is strongly affected by the presence of CTBN beyond 15%, and, thus, these two concomitant effects explain that the 17 and 20% CTBN materials are so brittle, more than the pure network.

This study exhibits a new parameter in the impact toughness of rubber-epoxy networks: the modification of the network itself, due to the presence of a large amount of CTBN.

In this complex chemical system, with DDA as curing agent, the morphology of the rubber domains is the result of a competition between the phase separation and the crosslinking kinetics. Further investigations will deal with the influence of the stoichiometric ratio and cure cycle on the morphology of the final material, in connection with mechanical properties.

References

1. C. B. Bucknall, *Toughened Plastics*, Applied Science, London, 1977.
2. J. N. Sultan and F. J. McGarry, *Polym. Eng. Sci.*, **13**, 29-34 (1973).
3. C. K. Riew, E. M. Rowe, and A. R. Siebert, *Toughness and Brittleness of Plastics*, R. D. Deanin and A. H. Grugnola Ed., *Adv. Chem. Series 154*, Am. Chem. Soc., Washington, DC, 1976, pp. 326-343.
4. L. T. Manzione, J. K. Gillham, and C. A. McPherson, *J. Appl. Polym. Sci.*, **26**, 2391-2401 (1981).
5. E. H. Rowe, A. R. Siebert, and R. S. Drake, *Mod. Plast. Aug.*, **49**, 110 (1970).
6. W. O. Bascom, R. L. Cottingham, R. L. Jones, and P. Peyser, *J. Appl. Polym. Sci.*, **19**, 2545-2567 (1975).
7. R. J. Morgan, E. T. Mones, and W. J. Steele, *Polymer*, **23**, 295-305 (1982).
8. A. C. Meeks, *Polymer*, **15**, 675-681 (1974).
9. W. D. Bascom, R. L. Cottingham, and C. O. Timmons, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **32**, 165-188 (1977).
10. S. A. Zahir, Third International Conference in Org. Coat. Sci. Tech., Athens, 1980.
11. J. Galy, Q. T. Pham, and J. P. Pascault, (1985), to appear.
12. Y. S. O, G. Merle, C. Pillot, and H. Sautereau, *Polym. Testing*, **5**, 37-43 (1985).
13. A. R. Siebert and C. K. Riew, *Am Chem. Soc., Org. Coat. Plast. Div.*, **31**, 552 (1971).
14. Y. G. Lin, H. Sautereau, and J. P. Pascault, 4 Journ e Nationale sur les Composites. Sep. 1984, Paris, pp. 569-581.
15. T. T. Wang and M. M. Zupko, *J. Appl. Polym. Sci.*, **26**, 2391-2401 (1981).
16. S. Kunz-Douglas, P. W. R. Beaumont, M. F. Ashby, *J. Mater. Sci.*, **15**, 1109-1123 (1980).
17. T. G. Fox, *Bull. Am. Phys. Soc.*, **1**, 123 (1956).
18. F. N. Kelley, F. Buesche, *J. Polym. Sci.*, **50**, 549-556 (1961).
19. P. R. Couchmann, *J. Am. Chem. Soc.*, **6**(11), 1156-1167 (1978).
20. G. C. Adams and T. K. Wu, *SPE 80 ANTEC*, 185 (1981).
21. C. B. Bucknall, T. Yoshii, *Br. Polym. J.*, **10**, 53-55 (1978).
22. M. Rink, T. Ricco, W. Lubery, and A. Pavan, *J. Appl. Polym. Sci.*, **22**, 429-443 (1978).

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